Colligative properties of solutions

We might expect the presence of solute particles to make the physical properties of solution different from those of the pure solvent. However, what we might not expect is that, in the case of four important solution properties, the ***number*** of solute particles makes the difference, not their chemical identity. These properties, known as colligative proprerties (colligative means “collective”), are:

1. vapor pressure lowering,
2. boiling point elevation,
3. freezing point depression,
4. Osmotic pressure.

Even though most of these effects are small, they have many practical applications, including some that are vital to biological systems.

Historically, colligative properties were measured to explore the nature of a solute in aqueous solution and its extent of dissociation into ions. Recall that an aqueous solution of an electrolyte conducts a current because the solute separates into ions as it dissolves. Soluble salts, strong acids, and strong bases dissociates completely. Their solutions conduct a large current, so these solutes are ***strong electrolytes***. Weak acids and weak bases dissociate very little. They are ***weak electrolytes*** because their solutions conduct little current. Many compounds, such as sugar and alcohol, do not dissociate into ions at all. They are ***non-electrolytes*** because their solutions do not conduct a current.

To predict the magnitude of a colligative property, we refer to the solute formula to find the number of particles in solution.

Each mole of non-electrolyte yields 1 mol of particles in the solution. For example, 0.35M glucose contains 0.35 M of solute particles per liter. In principle, each mole of strong electrolyte dissociated into the number of moles of ions in the formula unit: 0.4 M Na_2SO_4 contains 0.8 mol Na^+ ions and 0.4 mol SO_4^{2-} ions, or 1.2 mol of particles, per liter.

Colligative properties of nonvolatile non-electrolyte solutions

Let us examine the colligative properties of solutes that ***do not dissociate*** into ions and have negligible vapor pressure even at the boiling point of the solvent. Such solutes are called ***nonvolatile nonelectrolytes***; sucrose (table sugar) is an example. Later, we briefly explore the properties of volatile nonelectrolytes and of strong electrolytes.

1. **Vapor pressure lowering** The vapor pressure of a solution of a nonvolatile nonelectrolytes is always lower than the vapor pressure of the pure solvent. We can understand this *vapor pressure lowering (* ΔP) in terms of opposing rates and in terms of changes in entropy.

   Consider a pure solvent and the opposing rates of vaporization (molecules leaving the liquid) and of condensation (molecules reentering the liquid). At equilibrium, the two rates are equal. When we add some nonvolatile solute, the number of solvent molecules on the surface is lower, so fewer vaporize per unit time. To maintain equilibrium, fewer gas molecules can enter the liquid, which occurs only if the concentration of gas, that is, the vapor pressure, is lowered. In terms of the entropy change, recall that natural processes occur in a direction of increasing entropy. A pure solvent vaporizes because the vapor has a greater entropy than the liquid. However, the solvent in a solution already has a greater than it does as pure solvent, so it has less tendency to vaporize in order to gain entropy. Thus, by either argument, equilibrium is reached at a lower vapor pressure for the solution.

In quantitative terms, we find that the vapor pressure of solvent above the solution ($P_{solvent}$) equals the mole fraction of solvent in the solution ($X_{solvent}$) times the vapor pressure of the pure solvent ($P^{\circ}_{solvent}$). This relationship is expressed by **Raoult's law:**

$$P_{solvent} = X_{solvent} \times P^{\circ}_{solvent}$$

In a solution, $X_{solvent}$ is always less than 1, so $P_{solvent}$ is always less than $P^{\circ}_{solvent}$.

An ideal solution is one that follows Raoult's law at ***any concentration***. However, just as most gases deviate from ideality, so do most solutions. In practice, Raoult's law gives a good approximation of the behavior of ***dilute*** solutions only, and it becomes exact at infinite dilution.

How does the *amount* of solute affect the *magnitude* of the vapor pressure lowering, ΔP? The solution consists of solvent and solute, so the sum of their mole fractions equals 1:

$$\mathbf{X}_{solvent} + \mathbf{X}_{solute} = 1; thus\ , \mathbf{X}_{solvent} = 1 - \mathbf{X}_{\mathbf{solute}}$$

From Raoult’s law, we have

$$\boldsymbol{P}_{solvent} = \boldsymbol{X}_{solvent} \times \boldsymbol{P}^{\circ}_{solvent} = (\mathbf{1} - \mathbf{X}_{\mathbf{solute}}) \times \boldsymbol{P}^{\circ}_{solvent}$$

Multiplying through on the right side gives

$$\boldsymbol{P}_{solvent} = \boldsymbol{P}^{\circ}_{solvent} - (\boldsymbol{X}_{solvent} \times \boldsymbol{P}^{\circ}_{solvent})$$

Rearranging and introducing ΔP gives

$$P^{o}_{solvent} - P_{solvent} = \Delta P = X_{solute} \times P^{o}_{solven}$$

Thus, the *magnitude* of ΔP equals the mole fraction of solute times the vapor pressure of the pure solvent-a relationship applied in the next problem.

Sample problem Using Raoults’s law to find Vapor Pressure Lowering

Problem Calculate the vapor pressure lowering, ΔP, when 10.0 mL of glycerol ($C_3H_8O_3$) is added to 500. mL of water at $50.\,^{\circ}C$ .At this temperature, the vapor pressure of pure water is 92.5 torr and its density id 0.988 g/mL. The density of glycerol is 1.26 g/mL.

Solution calculating the amount (mol) of glycerol and of water:

$$Moles\ of\ glycerol = 10.0mL\ glycerol \times \frac{1.26g\ glycerol}{1\ mL\ glycerol} \times \frac{1\ mol\ glycerol}{92.09\ g\ glycerol}$$

$$= 0.137\ mol\ glycerol$$

$$moles\ of\ H_2o = 500.\,mL\ H_2O \times \frac{0.988\ gH_2O}{1\ mLH_2O} \times \frac{1\ molH_2O}{18.02\ g\ H_2O} = 27.4\ mol\ H_2O$$

Calculating the mole fraction of glycerol:

$$X_{glycerol} = \frac{0.137\ mol}{0.137mol + 27.4mol} = 0.00498$$

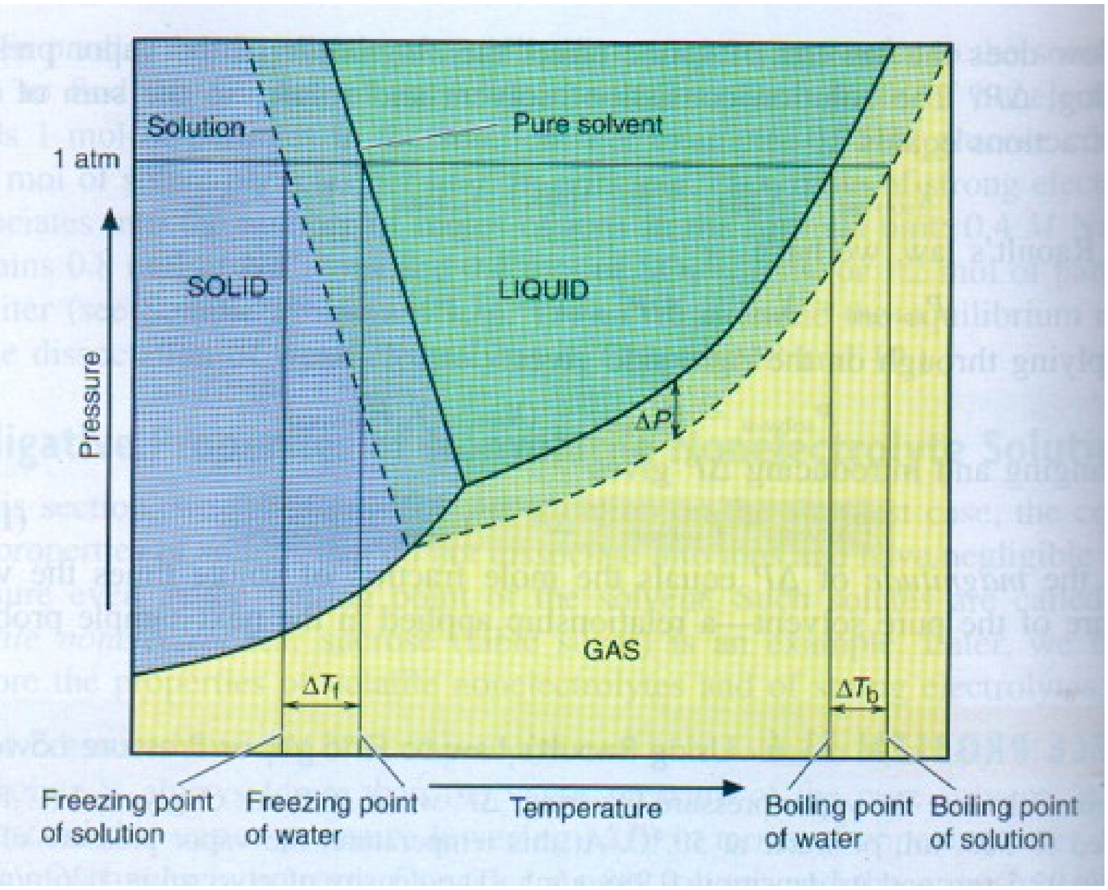
Finding the vapor pressure lowering:

$$\Delta P = X_{glycerol} \times P^{\circ}_{H_2O} = 0.00498 \times 92.5torr = 0.461\ torr$$

Follow-up problem (DO THIS PROBLEM ALONE)

Calculate the vapor pressure lowering of a solution of 2.00 g of aspirin ($\mathrm{M} = 180.15\ \mathrm{g/mol}$) in 50.0 g of methanol (CH_3OH) at 21.2$^{\circ}C$. Pure methanol has a vapor pressure of 101 torr at this temperature.

2. **Boiling Point Elevation** A *solution boils at a higher temperature than the pure solvent.* Let's see why. The boiling point (boiling temperature, T_b) of a liquid is the temperature at which ***its vapor pressure equals the external pressure***. The vapor pressure of a solution is lower than the external pressure at the solvent's boiling point because the vapor pressure of a solution is lower than that of the pure solvent at any temperature. Therefore, the solution does not yet boil. A higher temperature is needed to raise the solution's vapor pressure to equal the external pressure. We can see this **boiling point elevation (**ΔT_b)by superimposing a phase diagram for the solution on a phase diagram for the pure solvent, as shown below. Note that the gas-liquid line for the solution lies *below* that for the pure solvent at any temperature and to the right of it at any pressure.



Like the vapor pressure lowering, the magnitude of the boiling point elevation is proportional to the concentration of solute particles:

$$\Delta T_b \propto m \quad or \quad \Delta T_b = K_b m$$

Where m is the solution molality, K_b is the *molal boiling point elevation constant,* and ΔT_b is the boiling point elevation. We typically speak of K_b as a positive value, so we subtract the lower temperature from the higher; that is, we subtract the solvent T_b from the solution T_b.

$$\Delta T_b = T_{b(solution)} - T_{b(solvent)}$$

Molality is the concentration term used because it is related to mole fraction and thus to particles of solute. It also involves mass rather than volume of solvent, so it is not affected by temperature changes. The constant K_b has units of degrees Celsius per molal unit (°C/m) and is specific for a given solvent (Table 13.6).

Notice that the K_b for water is only 0.512 °C/m, so the changes in boiling point are quite small: if you dissolved 1.00 mol of glucose (180.g; 1.00 mol of particles) in 1.00 kg of water, or 0.500 mol of NaCl (29.2 g; a strong electrolyte, so also 1.00 mol of particles) in 1.00 kg of water, the boiling points of the resulting solutions at 1 atm would be only 100.512 °C instead of 100.000 °C.

Solvent	Boiling point (°C)	K_b (°C /m)	melting point (°C)	K_f (°C /m)
16.6	117.9	3.07		3.90
Bdnzene	80.1	2,53	5.5	4.90
Chloroform	61.7	3.63	-63.5	4.70
Ethanol	78.5	1.22	-117.3	1.99
Water	100.0	.512	0.0	1.86

3. **Freezing Point Depression** Remember that, only solvent molecules can vaporize from the solution, so molecules of the nonvolatile solute are left behind. Similarly, in many cases, *only solvent molecules can solidify,* again leaving solute molecules behind to form a slightly more concentrated solution. The freezing point of a solution is that temperature at which its vapor pressure equals that of the pure solvent. At this temperature, the two phases—solid solvent and liquid solution –are in equilibrium. Because the vapor pressure of the solution is lower than that of the solvent at any temperature, the solution freezes at a lower temperature than the solvent. In other words, the numbers of solvent particles leaving and entering the solid per unit time become equal at a lower temperature. The **freezing point depression** (ΔT_f) is shown in previous figure ; note that the solid-liquid line for the solution lies to the left of that for the pure solvent at any pressure.

   Like ΔT_f, the freezing point depression has a magnitude proportional to the molal concentration of solute:

   $$\Delta T_f \propto m \quad or \quad \Delta T_f = K_f m$$

Where K_f is the *molal freezing point depression constant,* which also has units of °C/m

Also like ΔT_b,

ΔT_f is considered a positive value, so we subtract the lower temperature from the higher; in this case, however, it is the solution ΔT_f

from the solvent ΔT_f:

$$\Delta T_f = T_{b(solution)} - T_{b(solvent)}$$

Here, too, the overall effect in aqueous solution is quite small because the K_f value for water is small—only 1.86 $^{\circ}\mathrm{C}$/m. Thus, 1 *m* glucose, 0.5 *m* NaCl, and 0.33 *m* K_2SO_4, all solutions with 1 mol of particles per kilogram of water, freeze at –1.86 $^{\circ}\mathrm{C}$ at 1 atm instead of at0.00 $^{\circ}\mathrm{C}$.

Sample problem determining the boiling point elevation and freezing point depression of a solution

Problem You add 1.00 kg of ethylene glycol $(C_2H_6O_2)$ antifreeze to your car radiator, which contains 4450 g of water. What are the boiling and freezing points of the solution?

Solution Calculating the molality:

$$moles\ of\ (C_2H_6O_2) = 1.00\ kg(C_2H_6O_2) \times \frac{10^3\,\mathrm{kg}}{1\,\mathrm{kg}} \times \frac{1\ mol(C_2H_6O_2)}{62.07\ g\ (C_2H_6O_2)} = 16.1\ mol\ (C_2H_6O_2)$$

$$Molality = \frac{mol\ solute}{kg\ solvent} = \frac{16.1\ mol(C_2H_6O_2)}{4450\ g\ H_2O \times \frac{1\ kg}{10^3\ g}} = 3.62\ m(C_2H_6O_2)$$

Finding the boiling point elevation and $T_{b(solution)}$, with K_b=0.512 $^{\circ}\mathrm{C}/m$:

$$\Delta T_b = \frac{0.512^{\circ}\mathrm{C}}{m} \times 3.62\ m = 1.85^{\circ}\mathrm{C}$$

$$T_{b(solution)} = T_{b(solvent)} + \Delta T_b = 100.00^{\circ}\mathrm{C} + 1.85^{\circ}\mathrm{C} = 101.85^{\circ}\mathrm{C}$$

Finding the freezing point depression and $T_{f(solution)}$, with $K_f = 1.86^{\circ}\mathrm{C}/m$:

$$\Delta T_f = \frac{1.86^{\circ}\mathrm{C}}{m} \times 3.62\ m = 6.73^{\circ}\mathrm{C}$$

$$T_{f(solution)} = T_{f(solvent)} + \Delta T_f = 0.00°\text{C} - 6.73°\text{C} = -6.73°\text{C}$$

Follow-up problem DO IT YOURSELF ALONE

A 0.30 M solution of sucrose that is at 37$^{°\text{C}}$ has approximation the same osmotic pressure as blood does. What is the osmotic pressure of blood?

Colligative properties of Volatile Nonelectrolyte solutions

What is the effect on vapor pressure when the solute *is* volatile, that is, when the vapor consists of solute *and* solvent molecules? From Raoult's law, we know that

$$P_{solvent} = X_{solvent} \times P^{\circ}_{solvent} \text{ and } P_{solute} = X_{solute} \times P^{\circ}_{solute}$$

Where $X_{solvent}$ and X_{solute} refer to the mole fractions in the liquid phase.

According to Dalton's law of partial pressures, the total vapor pressure is the sum of the partial vapor pressures:

$$P_{total} = P_{solvent} + P_{solute} = \left(X_{solvent} \times P^{\circ}_{solvent}\right) + \left(X_{solute} \times P^{\circ}_{solute}\right)$$

Just as a nonvolatile solute lowers the vapor pressure of the solvent by making the mole fraction of the solvent less than 1, *the presence of each volatile component lowers the vapor pressure of the other* by making each fraction less than 1.

Let's examine this effect in a solution that contains equal amounts (mol) of benzene (C_6H_6) and toluene (C_7H_8): $X_{ben} = X_{tol} = 0.500$. At 25 °C, the vapor pressure of pure benzene (P°_{ben}) is 95.1 torr and that of pure toluene (P°_{tol}) is 28.4 torr; note that benzene is more volatile than toluene. We find the partial pressures from Raoult's law:

$$P_{ben} = X_{ben} \times P^{\circ}_{ben} = 0.500 \times 95.1 torr = 47.6\ torr$$

$$P_{tol} = X_{tol} \times P^{\circ}_{tol} = 0.500 \times 28.4 torr = 14{,}2\ torr$$

As you can see, the presence of benzene lowers the vapor pressure of toluene, and vice versa.

Does the composition of the vapor differ from that of the solution?

To see, let's calculate the mole fraction of each substance *in the vapor* by applying Dalton's law. Recall that $X_A = P_A/P_{total}$. Therefore, for benzene and toluene in the vapor,

$$X_{ben} = \frac{P_{ben}}{P_{total}} = \frac{47.6\ torr}{47.6\ torr + 14.2\ torr} = 0.770$$

$$X_{tol} = \frac{P_{tol}}{P_{total}} = \frac{14.2\ torr}{47.6\ torr + 14.2\ torr} = 0.230$$

The vapor composition is very different from the solution composition. The essential point to notice is that *the vapor has a higher mole fraction of the* ***more*** *volatile solution component.* The 50:50 ratio of benzene:toluene in the liquid created a 77:23 ratio of benzene:toluene in the vapor. Condense this vapor into a separate container, and that new *solution* would have 77:23 composition, and the new vapor above it would be enriched still further in benzene.

In the process of **fractional distillation,** this phenomenon is used to separate a mixture of volatile components. Numerous vaporization-condensation steps continually enrich the vapor, until the vapor reaching the top of the fractionating column consists solely of the most volatile component. Figure 13.29 shows how fractional distillation is used in the industrial process of petroleum refining to separate the hundreds of individual compounds in crude oil into a small number of “fractions” based on boiling point range.

Colligative properties of strong electrolyte solutions

When we consider colligative properties of strong electrolyte solutions, the solute formula tells us the number of particles. For instance, the boiling point elevation (ΔT_b) of 0.05 *m* glucose$(C_6H_{12}O_6)$, because NaCl should be twice that of 0.05 *m* glucose $(C_6H_{12}O_6)$, because NaCl dissociate into two particles per formula unit. Thus, we include a multiplying factor in the equations for the colligative properties of electrolyte soulutions. The *van’t Hoff factor (i),* named after the Dutch chemist Jacobus van’t Hoff (1852-1991), is the ratio of the measured value of the colligative property in the electrolyte solution to the *expected* value for a nonelectrolyte solution:

$$i = \frac{measured\ value\ for\ electrolyte\ solution}{expected\ value\ for\ nonelectrolyte\ solution}$$

To calculate the colligative properties of strong electrolyte solutions, we incorporate the van’t Hoff factor into the equation:

For vapor pressure lowering: $\Delta P = i(\boldsymbol{X}_{solute} \times \boldsymbol{P}^{\circ}_{solute})$

For boiling point elevation: $\Delta T_b = (K_b m)i$

For freezing point depression: $\Delta T_f = (K_f m)i$

For osmotic pressure: $\Pi = i(MRT)$

If strong electrolyte solutions behaved ideally, the factor *i* would be the amount (mol) of particles in solution divided by the amount (mol) of dissolved solute; that is, *i* would be 2 for NaCl, 3 for $Mg(NO_3)_2$, and so forth. Careful experiment shows, however that *most strong electrolyte solutions are **not** ideal.* For example, comparing the boiling point elevation for 0.050 *m* NaCl solution with that for 0.050 *m* glucose solution gives a factor *i* of 1.9, not 2.0:

$$i = \frac{\Delta T_b \ of\ 0.050\ m\ NaCl}{\Delta T_b\ of\ 0.050\ m\ glucose} = \frac{0.049°C}{0.026°C} = 1.9$$

The measured value of the van’t Hoff factor is typically *lower* than that expected from the formula. This deviation implies that the ions are not behaving as independent particles. However, we know from other evidence that soluble salts dissociate completely into ions. The fact that the deviation is greater with divalent and trivalent ions is a strong indication that the ionic charge is somehow involved

To explain this nonideal behavior, we picture ions as separate but near each other. Clustered near a positive ion are, on average, more negative ions, and vice versa. Figure shows each ion surrounded by an **ionic atmosphere** of net opposite charge. Through these electrostatic associations, each type of ion behaves as if it were “tied up,” so its concentration seems *lower* than it actually is. Thus, we often speak of an *effective* concentration, obtained by multiplying *i* by the *stoichiometric* concentration based on the formula. The greater the charge, the stronger the electrostatic associations, so the deviation from ideal behavior is greater for compounds that dissociate into multivalent ions.

At ordinary conditions and concentrations, nonideal behavior of solutions is much more common (and the deviations much larger) than nonideal behavior of gases, because the particles in solutions are so much closer together. Nevertheless, the two systems exhibit some interesting similarities. Gases display nearly ideal behavior at low pressures because the distances between particles are large. Similarly, van’t Hoff factors (*i)* approach their ideal values as the solution becomes more dilute, that is, as the distance between ions increase. In gases, attractions between particles cause deviations from the expected pressure. In solutions, attractions between particles cause deviations from the expected size of a colligative property. Finally, both real gases and real solutions, we use empirically determined numbers (van der Waal constant or van’t Hoff factors) to transform theories (ideal gas law or Raoult’s law) into more useful relations.